

Spectral Evidence for the One-Step Three-Electron Oxidation of Phenylsulfinylacetic Acid and Oxalic Acid by Cr(VI)

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ABSTRACT

The co-oxidation of a mixture of phenylsulfinylacetic acid (PSAA) and oxalic acid (OxH₂) by Cr(VI) in 20% acetonitrile-80% water (v/v) medium follows third order kinetics, first order, each with respect to PSAA, OxH₂ and Cr(VI). The reaction involves nucleophilic attack of sulfur atom of PSAA on chromium of the oxidizing species, Cr(VI)-OxH₂ to form a ternary complex, Cr(VI)-OxH₂-PSAA followed by a one-step three-electron reduction of Cr(VI) to Cr(III) and simultaneous oxidation of both the substrates. The reaction is catalysed by Mn²⁺ ion while retarded by Al³⁺ ion. Electron releasing substituents in the meta- and para-positions of the phenyl ring of PSAA enhance the rate of co-oxidation while electron withdrawing substituents retards the reaction. The Hammett plots at different temperatures exhibit excellent correlation with negative ρ values. The reaction series obey isokinetic relationship and the observed isokinetic temperature is lying below the experimental range of temperature.

Keywords: Phenylsulfinylacetic Acid; Oxalic Acid; Co-Oxidation; Nucleophilic Attack of Sulfur; Three-Electron Transfer; Substituent Effect

1. Introduction

Oxalic acid acts as an efficient catalyst and enhances the rate of Cr(VI) oxidation of many inorganic [1-3] and organic compounds [4-10]. The oxalic acid catalysed processes involve the formation of Cr(IV)/Cr(V) intermediate species depending on the substrate, nature of Cr(VI) oxidizing reagent and experimental conditions. However, in the Cr(VI) co-oxidation of alcohol and oxalic acid, Rocek and co-workers [11] observed a direct reduction of Cr(VI) to Cr(III) without the formation of these intermediate species of chromium. In co-oxidation, oxalic acid undergoes oxidation in a stoichiometric ratio yielding CO₂ along with the other reductants with tremendous rate acceleration. Such type of rate enhancement with oxalic acid by Cr(VI) is observed with diverse substrates like formic acid [12], aromatic anils [13], anilides [14], cycloalkanones [15] and cinnamic acids [16].

Since the co-oxidation process offers the possibility of several synthetic applications, Cr(VI) co-oxidation stud-

ies are of striking significance. Srinivasan *et al.* [17] reported the co-oxidation of phenylmethyl sulfoxides and oxalic acid with Cr(VI) and designed the mechanism for the reaction which also highlights the substituent effect. Das *et al.* [18] monitored the micellar effect on the co-oxidation of dimethyl sulfoxide and oxalic acid by Cr(VI) considering it as a probe for three-electron transfer in a single step. In the case of co-oxidation of S-phenylmercaptoacetic acid and oxalic acid with pyridinium chlorochromate [19], two different mechanisms, based on substrate concentration, have been suggested. The significant utility of phenylsulfinylacetic acid (PSAA) in various synthetic routes [20-26] prompted the present investigation. Detailed literature scanning also reveals that there is no systematic kinetic report on PSAA and so, the present study of Cr(VI) co-oxidation of PSAA with oxalic acid (OxH₂) is undertaken and its salient features along with the substituent effects are discussed.

2. Experimental

The substrate, phenylsulfinylacetic acid and several meta-

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and para-substituted PSAAs were synthesized from the corresponding phenylmercaptoacetic acids by controlled oxidation with H_2O_2 [27], recrystallised from suitable solvents and their melting points were checked with the literature values [28]. The purity was further verified by LCMS. Potassium dichromate (BDH), sodium perchlorate (BDH), perchloric acid (Merck), oxalic acid (Merck), aluminium nitrate (Merck) and all other reagents were of AnalaR grade and they were used as such for the preparation of solutions of desired concentration for the kinetic study using double distilled water. Literature procedures were adopted for the purification of solvents, acetonitrile and water.

2.1. Kinetic Measurements

The kinetic study was performed under pseudo-first order conditions by maintaining $[\text{PSAA}], [\text{OxH}_2] \gg [\text{Cr(VI)}]$, in 20% acetonitrile-80% water mixture (v/v) and the progress of the reaction was observed by monitoring the decay of Cr(VI) at 351 nm at different time intervals with an ELICO Double Beam UV-vis Bio-spectrophotometer with an inbuilt thermostat. **Figure 1** shows the spectral changes recorded during the reaction.

The pseudo-first order rate constant (k_1) for each kinetic run was evaluated from the slope of the linear plot of log OD vs time by the method of least squares. The second order rate constant (k_2) was calculated from the relation: $k_2 = k_1/[\text{PSAA}]$. The precision of the k values is given in terms of 95% confidence limits of Students' t test.

2.2. Product Analysis

To characterize the products of the reaction, the reaction mixture containing excess of Cr(VI) over PSAA and OxH_2 was kept for 48 hours for completion of the reaction and then extracted with ether. The ether extract was

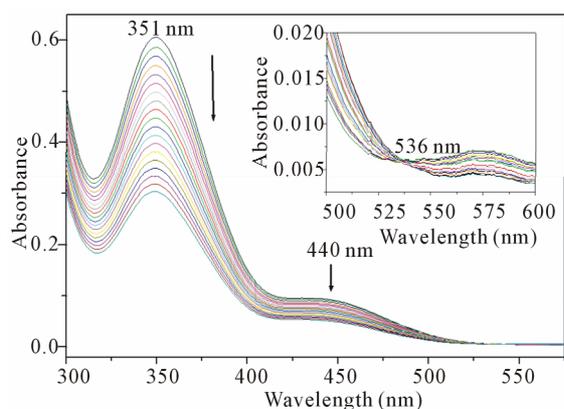


Figure 1. UV-visible spectra at different time intervals for the reaction of Cr(VI) with PSAA and OxH_2 in 20% acetonitrile-80% H_2O (v/v) $[\text{PSAA}] = 3.0 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$; $[\text{OxH}_2] = 1.0 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$; $[\text{Cr(VI)}] = 3.0 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$; $[\text{H}^+] = 7.5 \times 10^{-1} \text{ mol}\cdot\text{dm}^{-3}$.

collected, dried over anhydrous sodium sulfate and the solvent was removed by evaporation. The residue obtained from the ether extract was dried and subjected to GC-MS (**Figure 2**) and LC-MS (Supplementary Material: **Figure F1**) analysis. The parent peak at $m/z = 156$ in GC-MS and the peak eluted in LC-MS at a retention time of 1.87 min ionizes in APCI (+) mode with an area of 86% corresponding to the mass 157 indicate that methylphenyl sulfone is the sole product formed. The presence of strong IR bands (Supplementary Material: **Figure F2**) at 1148 cm^{-1} and 1290 cm^{-1} characteristic of symmetric and asymmetric stretching respectively of $>\text{SO}_2$ group further supports the formation of the product, methylphenyl sulfone.

The final fate of chromium (VI) can be predicted from the UV-visible spectroscopy by scanning the aqueous extract of the product mixture and comparing the spectral changes observed with that of authentic sample of Cr(III). The two UV-vis peaks of Cr(III) at 421 nm and 592 nm (**Figure 3(a)**) which were assigned to its octahedral transitions, ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{F})$ and ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ [29,30] were found to shift to lower wavelength regions, 414 nm and 562 nm for the product mixture (**Figure 3(b)**). This observation clearly indicates the existence of chromium as Cr(III) in the form of complex species probably with oxalic acid as observed by other researchers [31,32] and not exist as free ion.

3. Results and Discussion

The order of the reaction with respect to Cr(VI) is unity under pseudo-first order conditions of



which is clear from the linear plots of logOD vs time even upto 75% completion of reaction and constant pseudo-first order rate constant values. However, it is observed that in the lower regions of $[\text{Cr(VI)}]$, the pseudo-first order rate constant increases with decrease in $[\text{Cr(VI)}]$

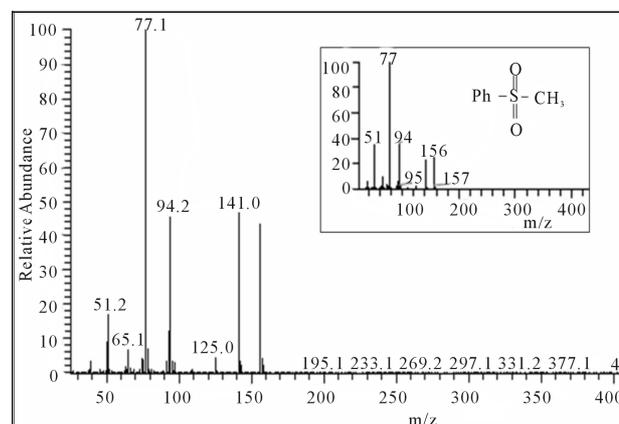


Figure 2. GC-MS spectrogram of the product.

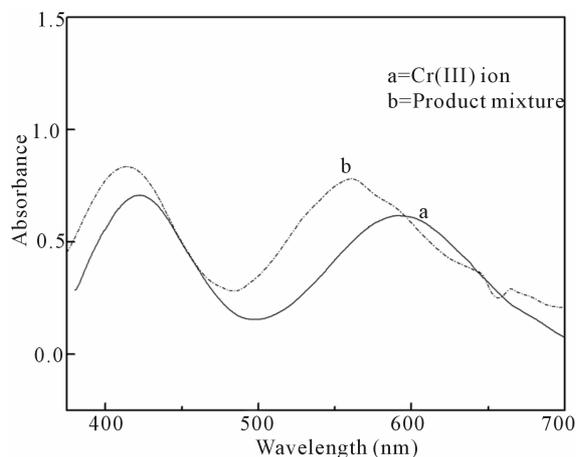


Figure 3. UV-vis spectra of the product mixture.

(**Table 1**). Such type of decrease in rate with increase in $[\text{Cr(VI)}]$ has been observed by several researchers [33-36]. However, the rate constants remain constant at higher concentration range of Cr(VI) . The decrease in rate with increase in Cr(VI) in lower concentration region may be due to the dimerization of Cr(VI) followed by decrease in concentration of active species [33-35] or due to the existence of some sort of weak association between monomeric Cr(VI) species [36].

The reaction is first order each in PSAA and oxalic acid, which are evidenced from the constant values obtained by dividing k_1 by $[\text{PSAA}]$ or $[\text{OxH}_2]$ and also from the unit slope of their respective log-log plots of k_1 vs $[\text{PSAA}]$ and $[\text{OxH}_2]$. The co-oxidation rate increases linearly with increase in $[\text{H}^+]$ (Supplementary material: **Table T1**) and shows a first order dependence with respect to $[\text{H}^+]$. This shows the protonation of Cr(VI) species in the experimental conditions which enhances the electrophilic activity of the oxidant. Solvent variation of the medium from 10% to 80% acetonitrile shows an accelerating effect with decrease in dielectric constant of the medium (Supplementary material: **Table T1**).

The effect of Mn^{2+} on rate (Supplementary material: **Table T2**) indicates that the rate of co-oxidation increases linearly with increase in $[\text{Mn}^{2+}]$ which is contrary to the retardation effect of Mn^{2+} on Cr(VI) oxidation due to the removal of Cr(IV) intermediate by Mn^{2+} . The observed acceleration effect not only excludes the involvement of Cr(IV) intermediate in this reaction but also indicates that Mn^{2+} acts as a catalyst. Such type of Mn^{2+} catalysis during co-oxidation process is witnessed by several authors [14,15,17]. Suppression of rate by the addition of aluminium nitrate (Supplementary material: **Table T2**) may be visualized due to the removal of OxH_2 by Al^{3+} .

3.1. Substituent Effect

The effect of substituents on the rate of co-oxidation is

examined with several meta- and para-substituted PSAAs at three different temperatures viz., 15°C , 20°C and 30°C . The second order rate constants and the activation parameters calculated from the Eyring's plot are enumerated in **Table 2**. To have a better insight into the contribution of substituent effect on the rate and mechanism, the rate constants were correlated with Hammett σ constants and found that an excellent correlation is obtained with negative ρ values (Supplementary material: **Figure F3**).

An analysis of the data in respect of linear free energy relationships reveals that the reaction series obeys isokinetic relationship as per the equation,

$$\Delta H^\ddagger = \Delta H_0 + \beta \Delta S^\ddagger$$

where, β is the isokinetic temperature, at which all the substituents in a given series have the same reactivity. Though the Petersen's [37] error criteria ($\Delta \Delta H^\ddagger \gg 2\delta$; δ is the maximum possible error in ΔH^\ddagger) is satisfied, the plot of ΔH^\ddagger vs ΔS^\ddagger gives only a bad correlation ($r = 0.861$). However, Exner's plot [38] of $\log k_2$ at 35°C against $\log k_2$ at 20°C correlate excellently ($r = 0.998$) and the slope of the plot (b) affords the isokinetic temperature, β .

$$\beta = T_1 T_2 (b - 1) / (b T_2 - T_1).$$

The isokinetic temperature computed from the above equation, 169.5 K is below the experimental temperature showing that the reaction is of entropy controlled. The linearity of Hammett plot and Exner's plot, evidence the involvement of same mechanism in all substituted PSAAs.

3.2. Mechanism

The existence of active Cr(VI) species in the reaction mixture depends mostly on the concentration of H^+ and Cr(VI) . In aqueous acidic solution, the various possible forms of Cr(VI) species are H_2CrO_4 , HCrO_4^- and HCrO_3^+ [39,40]. The species, HCrO_4^- exists only at very low concentration of H^+ [41] and hence under the maintained experimental conditions of H^+ the participation of HCrO_4^- is excluded. At higher concentrations of H^+ , the existence of Cr(VI) in the form HCrO_3^+ has been proved by several researchers [35,42,43] and on this basis its participation in the present co-oxidation process is envisaged. The positive slope obtained from the linear plot of $\log k_1$ vs $1/D$ along with first order dependence on $[\text{H}^+]$ supplement the involvement of a positively charged Cr(VI) species in the rate determining step.

The kinetic results revealed that the co-oxidation of phenylsulfinylacetic acid and oxalic acid by Cr(VI) follows the rate law,

$$-d[\text{Cr(VI)}]/dt = k[\text{PSAA}][\text{OxH}_2][\text{H}^+][\text{Cr(VI)}]$$

Table 1. Rate constants for the co-oxidation of PSAA and OxH₂ by Cr(VI).

10 ² [PSAA] (mol·dm ⁻³)	10 ⁴ k ₁ (s ⁻¹)	10 ⁴ [Cr(VI)] (mol·dm ⁻³)	^a 10 ⁴ k ₁ (s ⁻¹)	10 ² [OxH ₂] (mol·dm ⁻³)	^b 10 ⁴ k ₁ (s ⁻¹)
0	0.65 ± 0.07	0.5	32.7 ± 1.51	0	1.46 ± 0.04
0.8	2.76 ± 0.08	1.0	18.5 ± 0.37	1.0	3.22 ± 0.13
2.0	7.11 ± 0.23	2.0	15.8 ± 0.88	2.0	5.36 ± 0.26
3.0	10.4 ± 0.37	3.0	10.4 ± 0.37	3.0	7.52 ± 0.21
5.0	15.1 ± 0.34	4.0	11.8 ± 0.31	5.0	12.6 ± 0.24
9.0	27.2 ± 0.86	5.0	10.6 ± 0.54	7.0	18.8 ± 0.50
10	35.2 ± 0.98	6.0	11.3 ± 0.24	8.0	21.1 ± 0.64
20	60.6 ± 1.62			9.0	23.3 ± 1.20
				10	25.1 ± 0.70
				20	57.3 ± 1.50
				28	80.1 ± 3.00

[Cr(VI)] = 3.0 × 10⁻⁴ mol·dm⁻³; [OxH₂] = 1.0 × 10⁻² mol·dm⁻³; [H⁺] = 0.75 mol·dm⁻³; I = 0.8 mol·dm⁻³; solvent = 20% CH₃CN-80% H₂O (v/v); ^a[PSAA] = 3.0 × 10⁻² mol·dm⁻³; ^b[PSAA] = 1.0 × 10⁻² mol·dm⁻³.

Table 2. Second-order rate constants, enthalpy and entropy of activations for the co-oxidation of X-C₆H₄SOCH₂COOH and OxH₂ by Cr(VI).

X	10 ² k ₂ (mol ⁻¹ ·dm ³ ·s ⁻¹)			ΔH [#] (kJ·mol ⁻¹)	-ΔS [#] (JK ⁻¹ ·mol ⁻¹)
	20°C	30°C	35°C		
m-Br	0.98 ± 0.03	1.63 ± 0.06	1.96 ± 0.07	33.5 ± 3.4	169 ± 12
m-Cl	1.14 ± 0.03	1.97 ± 0.02	2.29 ± 0.05	33.6 ± 1.9	167 ± 6.8
m-F	1.24 ± 0.03	2.11 ± 0.03	2.59 ± 0.14	35.2 ± 3.1	161 ± 11
p-Cl	1.57 ± 0.09	2.61 ± 0.07	3.17 ± 0.03	34.1 ± 3.1	163 ± 11
p-Br	1.36 ± 0.03	2.39 ± 0.01	2.85 ± 0.09	36.2 ± 1.8	157 ± 6.3
p-F	2.05 ± 0.07	3.23 ± 0.03	3.99 ± 0.18	31.7 ± 2.9	169 ± 10
H	2.47 ± 0.09	4.33 ± 0.08	5.05 ± 0.21	34.2 ± 3.7	159 ± 13
m-CH ₃	2.69 ± 0.09	4.36 ± 0.04	5.39 ± 0.21	33.3 ± 2.7	161 ± 9.5
p-CH ₃	3.77 ± 0.16	5.72 ± 0.10	6.91 ± 0.15	28.6 ± 2.7	175 ± 9.5
p-OC ₂ H ₅	4.03 ± 0.16	6.29 ± 0.20	7.53 ± 0.16	29.8 ± 3.1	170 ± 11
p-OCH ₃	4.40 ± 0.29	6.58 ± 0.13	8.36 ± 0.21	30.0 ± 3.7	168 ± 13
ρ	-0.94 ± 0.03	-0.87 ± 0.03	-0.88 ± 0.03		
r	0.995	0.992	0.994		

[X-C₆H₄SOCH₂COOH] = 3.0 × 10⁻² mol·dm⁻³; [OxH₂] = 0.01 mol·dm⁻³; [Cr(VI)] = 3.0 × 10⁻⁴ mol·dm⁻³; [H⁺] = 0.75 mol·dm⁻³; I = 0.75 mol·dm⁻³; solvent = 40% CH₃CN-60% H₂O (v/v).

It has been reported that in the well-documented Cr(VI) oxidation of several substrates in the presence of oxalic acid, the cyclic form of an intermediate formed between Cr(VI) and oxalic acid is assumed to be the oxidizing species. Such complex formation between the oxidant and oxalic acid is indispensable for co-oxidation to occur [17]. In the present case too, addition of oxalic acid to

Cr(VI) leads to a substantial hyperchromic shift at 263 nm and 351 nm in the UV-vis spectra of Cr(VI) (**Figure 4(b)**) which indicates the involvement of Cr(VI) in complex formation. Based on the above facts, it has been proposed that HCrO₃⁺ forms a cyclic complex (C₁, **Scheme 1**) with oxalic acid in the first step of the mechanism. The rate acceleration is almost cancelled by the

addition of Al^{3+} ion which is a direct evidence for the difficulty in the formation of Cr(VI)-OxH_2 species as Al^{3+} removes OxH_2 . Further, broadening of the peak at 263 nm which merges with the peak at 351 nm (**Figure 4(d)**) is perceived during the addition of Al^{3+} ion to the reaction mixture.

In order to comprehend the subsequent steps in the mechanism of co-oxidation and the binding nature of PSAA with the oxidizing species, the UV-vis spectrum was recorded for the reaction mixture. The change in the shape as well as broadening of the peak at 263 nm in the presence of PSAA (**Figure 4(c)**) clearly reveals the formation of a new species probably termolecular intermediate complex, C_2 . The formation of this intermediate, $(\text{Cr(VI)-OxH}_2\text{-PSAA})$ as a result of nucleophilic attack of sulfur of PSAA on chromium atom of the Cr(VI)-OxH_2 complex is the rate determining step. The importance of this intermediate, C_2 during co-oxidation is known from the significant rate acceleration observed when both PSAA and OxH_2 co-exists than their individual rate constants with Cr(VI) under the same experimental conditions. The high negative entropy of activation for this co-oxidation system ($-158.88 \pm 12.8 \text{ JK}^{-1}\cdot\text{mol}^{-1}$) when compared to that of the reaction without oxalic acid ($-24.49 \pm 0.09 \text{ JK}^{-1}\cdot\text{mol}^{-1}$) suggests that there exists a highly ordered transition state in the rate

determining step.

As a result of electron transfer from sulfur of PSAA to chromium, a positive charge is developed on the sulfur center of the complex C_2 . The negative ρ value observed in the substituent effect study also confirms the existence

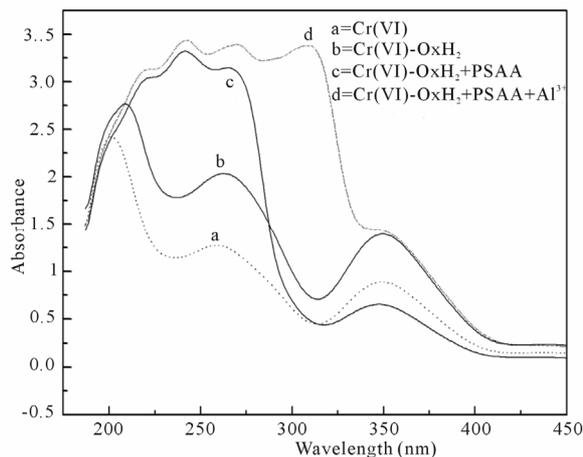
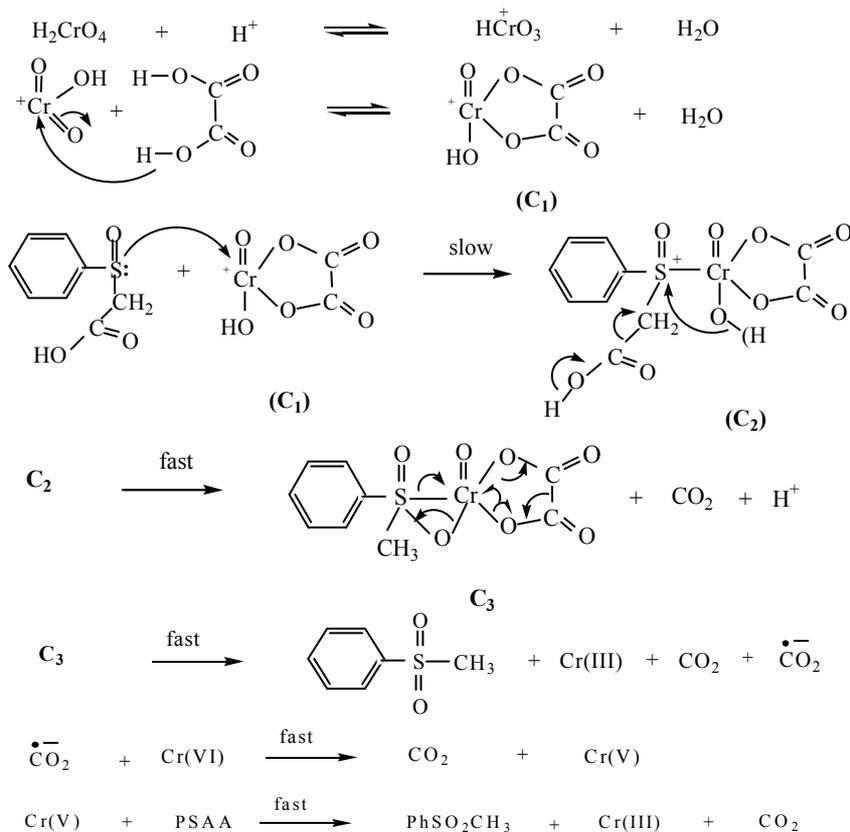


Figure 4. UV-vis spectra of (a) Cr(VI) alone (b) Cr(VI) and OxH_2 ; (c) Cr(VI) , OxH_2 and PSAA and (d) Cr(VI) , OxH_2 , PSAA and Al^{3+} [$\text{Cr(VI)}] = 3.0 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$; [$\text{PSAA}] = 3.0 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$; [$\text{OxH}_2] = 1.0 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$; [$\text{HClO}_4] = 7.5 \times 10^{-1} \text{ mol}\cdot\text{dm}^{-3}$; solvent = 20% CH_3CN -80% H_2O (v/v).



Scheme 1. Co-oxidation of PSAA and oxalic acid by Cr(VI) .

of sulfonium ion intermediate in the rate determining step. The presence of electron releasing groups in the PSAA increase the electron density on sulfur atom of PSAA which makes PSAA a more efficient nucleophile for binding with the positively charged oxidizing species, Cr(VI)-OxH₂. Besides, electron releasing substituents stabilize the intermediate, C₂ while electron withdrawing substituents in PSAA destabilize it. The rapid oxidation of PSAA-oxalic acid mixture by Cr(VI) supports that the reduction of Cr(VI) through a termolecular complex must be much more favourable and hence faster than their individual oxidation reactions.

The intermediate, C₂ then undergoes several fast steps including ligand coupling and decarboxylation from PSAA moiety leading to the formation of the products. During this process, Cr(VI) is directly reduced to Cr(III) by a one-step three-electron transfer which involves a two electron transfer from PSAA and a one electron transfer from oxalic acid. The direct evidence for the one-step three electron transfer, *i.e.*, reduction of Cr(VI) to Cr(III) arises from the existence of isobestic point at λ_{\max} 540 nm (**Figure 1**) in the overlay of the reaction mixture.

The involvement of OxH₂ as co-reductant and not as a catalyst in the reaction can be arrived from the amount of CO₂ liberated from the reaction. The number of moles of CO₂ liberated in the reactions with and without oxalic acid is determined quantitatively by the method described by Crossno *et al.* [44]. In the present reaction it has been observed that the amount of CO₂ liberated is more than one mole and this shows that CO₂ is liberated from oxalic acid too besides PSAA. The CO₂ thus formed may then undergo further rapid oxidation with Cr(VI) producing CO₂ and Cr(V). Then, Cr(V) reacts with another molecule of PSAA forming products.

4. Conclusion

The co-oxidation of phenylsulfinylacetic acid and oxalic acid by Cr(VI) follows three electron transfer mechanisms. The reduction of Cr(VI) to Cr(III) in a concerted step is assumed to be effective by the active oxidising species, Cr(VI)-OxH₂ via a termolecular complex, Cr(VI)-OxH₂-PSAA. The product analysis is also in support of the proposed mechanism.

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Supplementary Materials

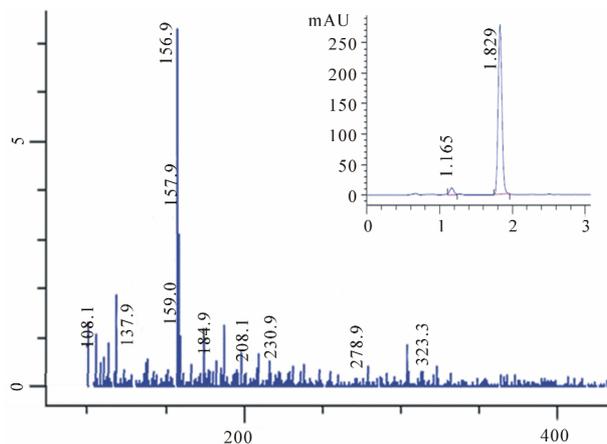


Figure F1. LC-MS analysis of the product.

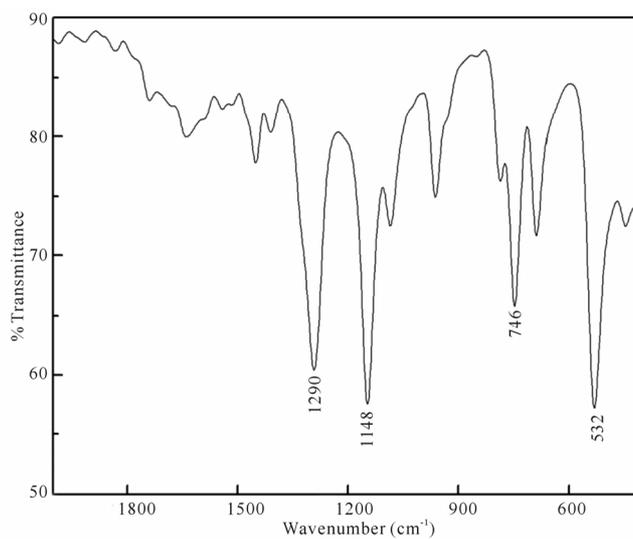


Figure F2. IR spectra of the product.

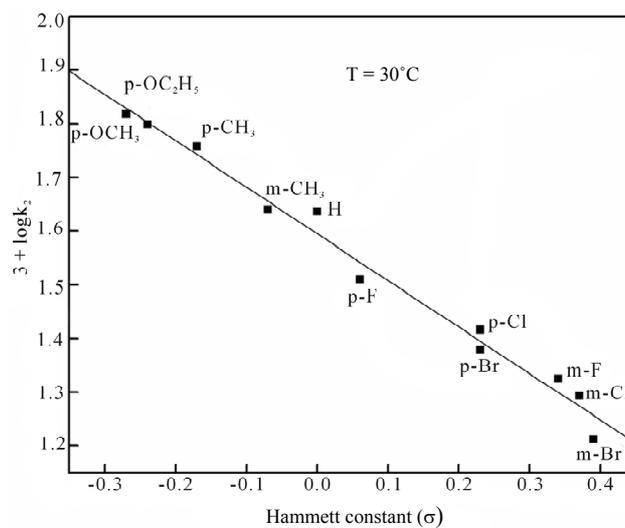


Figure F3. Hammett plot at 30°C.

Table T1. Effect of solvent composition, $[H^+]$ and ionic strength on rate constant at 30°C.

CH ₃ CN-H ₂ O (% v/v)	$10^4 k_1^a$ (s ⁻¹)	$10^1 [H^+]$ (mol·dm ⁻³)	$10^4 k_1^b$ (s ⁻¹)	I (mol·dm ⁻³)	$10^4 k_1^c$ (s ⁻¹)
10 – 90	9.43 ± 0.22	2.5	3.42 ± 0.10	0.8	10.4 ± 0.37
20 – 80	10.4 ± 0.37	5.0	6.70 ± 0.15	1.0	10.3 ± 0.21
30 – 70	11.9 ± 0.25	7.5	10.6 ± 0.30	1.2	10.4 ± 0.34
40 – 60	13.0 ± 0.35	10.0	13.3 ± 0.20	1.4	10.7 ± 0.25
50 – 50	16.5 ± 0.23	12.5	16.7 ± 0.32	1.55	10.1 ± 0.26
60 – 40	20.2 ± 0.46	15.0	19.9 ± 0.44	1.8	11.2 ± 0.30
70 – 30	27.6 ± 0.89	20.0	32.5 ± 1.61		
80 – 20	40.8 ± 1.30				

[Cr(VI)] = 3.0×10^{-4} mol·dm⁻³; [PSAA] = 3.0×10^{-2} mol·dm⁻³; ^{a,c}[H⁺] = 0.75 mol·dm⁻³; [OxH₂] = 1.0×10^{-2} mol·dm⁻³; ^aI = 0.8 mol·dm⁻³; ^bI = 1.1 mol·dm⁻³; ^{b,c}solvent = 20% CH₃CN-80% H₂O (v/v).

Table T2. Effect of Mn²⁺ ion and Al³⁺ ion on reaction rate.

$10^3 [Mn^{2+}]$ (mol·dm ⁻³)	^a $10^4 k_1$ (s ⁻¹)	$10^1 [Al^{3+}]$ (mol·dm ⁻³)	^b $10^4 k_1$ (s ⁻¹)
0	10.3 ± 0.21	0	10.4 ± 0.37
1.0	11.9 ± 0.36	0.05	9.43 ± 0.21
2.0	13.9 ± 0.45	0.1	8.58 ± 0.33
5.0	19.4 ± 0.59	0.2	5.73 ± 0.25
7.0	27.6 ± 0.89	0.3	3.24 ± 0.15
9.0	41.0 ± 1.50		
10	44.9 ± 1.10		

[Cr(VI)] = 3.0×10^{-4} mol·dm⁻³; [PSAA] = 3.0×10^{-2} mol·dm⁻³; [OxH₂] = 1.0×10^{-2} mol·dm⁻³; [H⁺] = 7.5×10^{-1} mol·dm⁻³; solvent = 20% CH₃CN-80% H₂O (v/v); ^aI = 1.0 mol·dm⁻³; ^bI = 2.55 mol·dm⁻³.